

# Ag catalyzed partial oxidation reactions investigated by *in-situ* photoelectron spectroscopy

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## Introduction

Ag is used by the chemical industry in two important catalytic oxidation reactions, formaldehyde synthesis and ethylene epoxidation [1]. The economic importance of these processes motivated an extensive investigation of the Ag-O system in past years [2-4]. However the mechanisms behind the remarkable selectivity obtained with Ag catalysts for both reactions is still focus of debate in the literature [5].

In this work we applied the recently developed *in situ* XPS technique to investigate the chemical state of the Ag catalyst surface in equilibrium with the gas phase under reaction conditions in the mbar pressure range and at industrially relevant temperatures.

## Experimental

In situ XPS experiments were performed using the high pressure endstation of ISSS beamline at synchrotron radiation facility BESSY II [6]. Catalysts were pressed as pellets and heated from the back side using an infrared laser system. The total pressure in the reaction chamber was kept at 0.50 mbar by a pressure controlled valve. The partial pressure of the gasses was regulated by calibrated mass flow controllers and the gas phase composition changes were monitored by an electron impact quadrupole mass spectrometer (MS), a proton transfer reaction MS (PTRMS) and a micro gas chromatograph (GC).

## Results/Discussion

Under pure O<sub>2</sub> atmosphere in the 150-500 C temperature range, five distinct features in the O1s XP spectra were identified and assigned to different atomic O species on Ag (figure 1-a). Evidences for the distinct electronic structure of these species were obtained by comparing their binding energies, temperature stability, amount of ionic Ag, valence band and Auger features. This analysis indicates that Ag is able to activate molecular oxygen into a number of distinct active forms with different chemical nature, which ultimately might lead to different roles in the oxidation reactions.

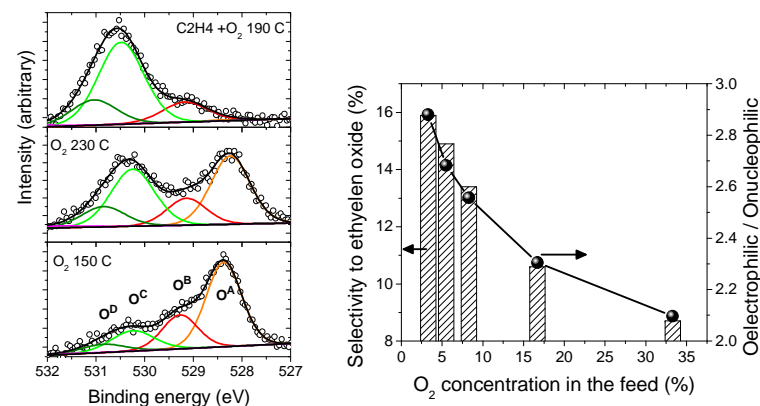


Figure 1. (a) O1s spectra showing the O species on Ag under different gas atmospheres and temperatures. (b) Correlation of the selectivity to ethylene oxide with the ratio of electrophilic and nucleophilic O species.

When methanol or ethylene is present together with O<sub>2</sub> in the gas phase, drastic changes in the O species distribution are observed, as a result of their different reactivity. Some of the species completely vanish, the abundance of others correlates with the hydrocarbon partial pressure. For the case of ethylene epoxidation running at steady state conditions, it was observed that the selectivity to the epoxide can be correlated to the ratio of different O species (figure 1b). A model of the role of the different O species in the frame of the oxidation reactions is suggested. Based on the electronic structure and reactivity data, it is proposed that while some species act as nucleophilic centers attacking C-H bonds (O<sup>A</sup> and O<sup>B</sup>), which is the first step to total oxidation, other act as an electrophilic agent, attacking the C=C bonds and producing the epoxide (O<sup>C</sup>).

## References.

1. B. K. Hodnet, *Heterogeneous Catalytic Oxidation*, Wiley, New York, 2000.
2. V.I. Bukhtiyarov, A.I. Nizovskii, H. Bluhm, M. Hävecker, E. Kleimenov, A. Knop-Gericke, R. Schlögl, *J. Catal.*, **238**, 260 (2006).
3. X. Bao, M. Muhler, Th. Schedel-Niedrig, R. Schlögl, *Phys. Rev. B*, **54**, 2246 (1996).
4. A. Michaelides, K. Reuter, M. Scheffler, *J. Vac. Sci. Technol. A*, **23**, 1487 (2005).
5. V. I. Bukhtiyarov, A. Knop-Gericke, *Ethylene epoxidation on silver catalysts*, in C. Hess, R. Schlögl, *Nanostructured catalysts: selective oxidation reactions*, in press
6. A. Knop-Gericke et al., *Adv. Cat.* **52**, 213 (2009).